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PETROLEUM-BASED SAFE PROCESS OILS IN NR AND NR/SBR BLENDS: EFFECTS OF OIL TYPES ON PROPERTIES OF CARBON BLACK FILLED COMPOUNDS

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ABSTRACT

There is a need for safe, low Polycyclic Aromatic Hydrocarbons containing process oils for replacement of toxic distillate aromatic extract (DAE) in rubber applications. Potential and commercially available petroleum-based safe process oils are: Treated Distillate Aromatic Extract (TDAE), Mildly Extracted Solvate (MES) and Naphthenics (NAP). This work investigates the influence of DAE-, TDAE- and MES-oils at different loadings on the properties of carbon-black reinforced NR and NR/SBR rubber compounds, typically applied in tires. The properties of the plasticized compounds are clearly affected by oil contents, but less dependent on oil types. The compounds with DAE oil have a lower Mooney viscosity but higher complex viscosity as well as higher Payne effect when compared to the mixes with

TDAE- and MES-oils. The replacement of DAE- with TDAE- and MES-oils in NR compounds has only small effects on the vulcanization characteristics and mechanical properties, but clearly influences the properties which are related to changes of the glass transition temperature and viscoelastic behavior: i.e. abrasion resistance, fatigue life, resilience, heat build-up and loss tangent. The lowest T_g of MES leads to the best elastic response in the NR vulcanizates, but TDAE gives the best overall elastic response for the NR/SBR blend vulcanizates.

Keywords: TDAE; MES; DAE, Natural Rubber; Styrene-Butadiene rubber; Tires

INTRODUCTION

Process oil is one of the compounding ingredients that are used in rubber formulations to improve processing behavior, low temperature properties and dispersion of fillers. Conventionally, highly aromatic oils (HA oils) are widely used in rubber compounds because they provide good compatibility with both natural and many synthetic rubbers. Carbon black is the most commonly used reinforcing filler for rubber compounds, including those used in tires. The incorporation of carbon black into rubber compounds improves various properties such as modulus, tensile and tear strength, fatigue life and abrasion resistance. To achieve the desired performance, carbon black must be sufficiently dispersed in the rubber, as poor dispersion leads to detrimental effects, e.g. reduced product life, poor processing characteristics and poor performance.[1] The filled rubber compounds are highly complex systems in which various solid and liquid ingredients must be dispersed in the rubber matrix.[2] In such a system, the reinforcing filler develops strong interactions that lead to a structural

material and associated specific flow properties.[2] Filler-rubber interactions give rise to additional crosslinks in the network structure, and immobilized elastomeric layers on the filler surface have an influence on the dynamic response of the materials.[3]

The incorporation of process oils reduces the compound viscosity, improves processing characteristics, facilitates filler dispersion, and helps to reduce the price of the compounds and resulting products. For carbon black filled tire compounds, highly aromatic oil or Distillate Aromatic Extract (DAE) was conventionally used due to its good compatibility with tire elastomers.[4] However, because of the toxicity of the high amounts of Polycyclic Aromatic Hydrocarbons (PAHs) in DAE-oil[5], low PAH-containing process oils have been developed as replacements for DAE, including Treated Distillate Aromatic Extract (TDAE), Mildly Extracted Solvate (MES), Naphthenic oils (NAP) and natural oils.

It has been reported that the use of petroleum-based safe process oils, such as TDAE, MES and NAP resulted in a narrow range of changes in rheological, physical and mechanical properties of un-aged vulcanizates of NR, SBR, NR/SBR and NR/brominated-isobutylene-isoprene rubber (BIIR).[6] The replacement of DAE by TDAE, MES and NAP in carbon black- and silica-filled tire compounds slightly shifted the wet grip performance and improved the rolling resistance, which was most clearly observed in carbon black-filled compounds.[7] Natural-based oils have also been investigated. NR, SBR and NR/SBR compounds plasticized with epoxidized palm oil (EPO), which showed comparable cure characteristics and processing properties, as well as mechanical and dynamic mechanical properties of the vulcanizates when compared to compounds with DAE oil.[8] Some natural oils were also reported to give better abrasion resistance in NR, NR/BR and S-SBR/NR/BR compounds, compared to DAE oil.[9]

The present work discusses the influence of DAE-, TDAE- and MES-oils at different loadings in HAF carbon black filled NR and NR/SBR compounds. NR based tire tread compounds are basically used for truck tires, but NR/SBR blends for passenger tire treads. The influences of oil types and contents on processing properties, cure characteristics, filler-filler interaction, mechanical and dynamic properties of carbon black-filled NR and NR/SBR compounds are investigated.

EXPERIMENTAL

MATERIALS

Natural rubber (Ribbed Smoked Sheet 3, RSS3) was locally produced in Vietnam. Styrene Butadiene rubber (Buna® SB 1502-Schkopau) was obtained from Styron HoldCo GmbH, Germany. Three types of oils, i.e. DAE (Tudalen 65), TDAE (Vivatec 500) and MES (Vivatec 200), were supplied by Hansen & Rosenthal KG (Hamburg, Germany). Carbon black N330 or HAF (VULCAN®) was obtained from Cabot Corporation, Alpharetta, Ga, USA. N-cyclohexyl-2-benzothiazolesulfenamide (CBS) and diphenyl guanidine (DPG) were obtained from Flexsys B.V., Belgium. Sulfur was obtained from Sigma Aldrich, Zwijndrecht, the Netherlands. The other compounding ingredients: stearic acid, zinc oxide, polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) and microcrystalline wax, were commercial grades for the rubber industry. All elastomers and compounding ingredients were used as received.

PREPARATION OF RUBBER COMPOUNDS

Compound preparation was carried out by using a two step-mixing procedure. In the first step, a rubber masterbatch was prepared by using an internal mixer with a chamber volume of 5 liters and intermeshing rotor system (Werner & Pfleiderer GK5E, Germany), a mixer temperature setting of 50°C, a fill factor of 0.70 and a rotor speed of 40 rpm. The formulations are given in Table I. The oil contents of the three different types of process oils, i.e. DAE, TDAE and MES were varied between 0, 5, 10 and 15 phr.

To minimize variation due to the mastication effect of NR and to homogenize the rubber after storage prior to being used, NR was pre-masticated for 3 mins on a two-roll mill with setting of the nip gap at 3 mm, and kept at room temperature overnight. The oils were heated to 60°C before being added into the mixer. For NR compounds, the mixing procedures in the internal mixer started with a re-mastication of the rubber for 1 min, followed by the addition of stearic acid, zinc oxide, 6PPD, TMQ, microcrystalline wax and 2/3 carbon black, and mixed for 3 mins. Subsequently, 1/3 carbon black and process oil were added and mixed for another 4 mins. After that, the masterbatch was discharged and made into a sheet on a two-roll mill. The first step mixing of the NR/SBR blends started by adding pre-masticated NR and SBR into the internal mixer and mixing for 2 mins, followed by the same mixing procedure as that of the NR compound.

The second mixing step for both compound types was to add the curatives, i.e. CBS, DPG and sulfur into the masterbatches by using a two-roll mill. The final compounds were sheeted to a thickness of approximately 3 mm.

TESTING OF UNCURED COMPOUNDS AND VULCANIZATION

Mooney viscosity test.–Mooney viscosity and Mooney stress relaxation were determined using a Mooney viscometer (MV2000vs, Alpha Technologies, USA) at 100°C and large rotor according to ASTM D1646.

Complex viscosity.–Complex viscosity of the uncured compounds was tested at a frequency of 0.5 Hz by using a Rubber Process Analyzer (RPA2000, Alpha Technologies) at 100°C and strain of 7%.

Payne effect.–Filler-filler interactions were characterized by strain sweep measurements to determine the change of storage modulus (G′) as a function of strain for the uncured compounds by using the RPA2000 at 100°C and a frequency of 0.5 Hz. The strains were varied in the range of 0.56% - 100%. The Payne effect was determined from the difference of G′ at 0.56% and 100%, i.e. G′(0.56%) - G′(100%).

Cure characteristics and vulcanization.–Cure characteristics were tested at 150°C for 30 mins. using the RPA2000 according to ASTM D5289, and the rubber compounds were vulcanized to their 90% optimum cure times by compression molding at 150°C.

TESTING OF RUBBER VULCANIZATES

Tensile properties.–The tensile properties were tested according to ISO 37 by using a Zwick Z1.0 tensile testing machine operated at a constant crosshead speed of 500 mm/min and dumb-bell test pieces type 2.

Abrasion resistance.–A DIN abrasion tester was employed to determine the volume loss in accordance with DIN53516.

Fatigue to failure.–Fatigue life of the specimens was tested using a Monsanto fatigue-to-failure tester as described in ASTM D4482. Dumbbell shaped specimens were stretched at

an extension ratio of 2.0 and subjected to a tensile strain cycle at 1.7 Hz. The number of cycles required to cause failure was recorded.

Rebound resilience.–A Dunlop tripsometer (Wallace Test Equipment, England) was used for measuring rebound resilience of the NR vulcanizates according to ISO 4662. The tests were carried out at 60°C, and resilience was calculated in percent according to equation (1):

$$\%\,\text{Resilience} = \frac{1-\cos B}{1-\cos A}\text{x}100 \qquad (1)$$

Where A is the angle at which the plunger was released (45 degrees), and B is the angle which the plunger bounced back to after hitting the specimen.

Heat build-up (HBU). –The test was performed by using a Goodrich Flexometer (Ferry Industry, USA) according to ASTM D623-07. A cylindrical shaped sample having a height of 25 mm and a diameter of 17.5 mm was tested at 100°C for 25 mins by applying a weight of 11 kg, stroke 4.45 mm and frequency of 30 Hz. The increase in temperature (ΔT) from the beginning of the test (T_0) to 25 mins test time (T_{25}) was recorded.

Dynamic mechanical properties.–Thin sheets of rubber vulcanizates with dimensions of 10 x 24 x 1 mm^3 were tested by using a dynamic mechanical thermal analyzer (Rheometrics Scientific DMTA V, USA) in the tension mode. The measurement was performed with a frequency of 10 Hz, a heating rate of 5 °C/min over a temperature range of -130 °C to +100 °C. In the range of -130 °C to -20 °C, the strain was set at 0.002%, and in the temperature range of -20 °C to +100 °C, a strain of 0.02% was applied.

RESULTS AND DISCUSSION

VISCOELASTIC PROPERTIES OF COMPOUNDS PRIOR TO VULCANIZATION

Mooneyviscosity.-Change of oil contents has a larger effect on the Mooney viscosities of the NR and NR/SBR compounds than change of oil types, as shown in FIG. 1. In the filled compounds, the cause of different viscosities may be related to the level of filler dispersion and mutual interactions between filler aggregates, interactions between fillers and rubber, and the mutual solubility between oils and rubber. DAE oil has a higher compatibility with both the NR and SBR rubbers than the TDAE- and MES-oils, as determined in a previous project from the smallest difference in solubility parameters ($\Delta\delta$) between rubbers and oils at high temperature (≥100°C).[4] A better rubber-oil compatibility and filler dispersion or less filler-filler interactions results in lower compound viscosities.[8] Therefore, the better compatibility between DAE oil and rubber is expected to lead to a more homogeneous mixture and helps the filler dispersion.

The NR filled-compounds with DAE oil show the lowest Mooney viscosities, the result of the highest plasticizing effect due to its best compatibility with the rubbers. It is interesting to note, that the first 5 phr of all oil types give a rise in Mooney viscosity relative to the compound without oil added, as observed in FIG. 1(a). This might be an artefact related to an extra mastication effect of NR during the mixing step. Without oil, higher shear forces are generated during mixing and the molecular chains are more broken down than if some oil is present, as NR is sensitive to this breakdown due to its reactive double bonds in the polymer backbone. As the molecular weight is strongly related to viscosity[2] and shorter chains have a higher mobility, so the viscosity of this compound is lower when compared to the compounds with a small amount of oil at 5 phr. The use of 5 phr of oil helps to lubricate the rubber chains

and carbon black particles/aggregates, so the shear forces generated during the mixing stage were lower than for the un-plasticized compound. The NR/SBR masterbatches with 5 phr of DAE- and TDAE-oils show similar Mooney viscosities and the one with MES oil shows a higher value when compared with the compound without oil, as shown in FIG. 1(b). The phenomenon of increased Mooney viscosity at 5 phr of oil loading is quite similar to what was observed for the HAF-filled NR compounds, but the difference of Mooney viscosities of the compounds without oil and with 5 phr of oil is smaller in the blend that has SBR as a component, because SBR is not sensitive to mastication like NR. Further increase of the oil contents to 10 and 15 phr decreases the Mooney viscosity of the compounds, mainly owing to the plasticization and lubrication effects.

Mooney relaxation.-The Mooney stress relaxation can be described by the equation:

$$M = K.t^{\alpha} \qquad (2)$$

where M is the torque in Mooney units, t is the time after stopping the rotor, and K is a constant equal to the torque in Mooney units 1 sec. after the rotor has stopped, α is an exponent that measures the rate of stress relaxation. A higher decay rate means a higher ratio of the viscous over elastic properties, and a lower uncured rubber elasticity.[10,11] As displayed in FIG. 1(a), increasing oil contents result in a flatter slope, i.e. a lower rate of decay, of the NR compounds except for the ones with 5 phr of again. This indicates that the oils enhance the relative uncured rubber elastic response which could be attributed to chain flexibility in the presence of oil in between the rubber molecules. The DAE oil gives the lowest decay rate (i.e. the number is less negative) at the same oil contents due to its good compatibility with NR, which makes facilitates rubber chain movement and interactions with fillers. The NR/SBR blends consisting of different oil types and loadings show the same trends of Mooney stress

relaxation rate as those of the filled-NR compounds. Carbon black filled NR/SBR compounds with DAE-oil tend to have a lower rate of decay especially at 5 phr, where the decay rate may be ranked according to the oil types as follows: MES > TDAE > DAE. DAE-oil is more compatible with both of NR and SBR rubbers than the other two oils, so the interaction between the plasticized rubber and filler aggregates is better and the rubber chains move easier providing a larger elastic/viscous ratio of the uncured compounds. Increasing oil contents tend to give lower stress relaxation rates of the NR/SBR compounds, indicating increased uncured elasticity in the presence of the oils.

Complex viscosity.-The complex viscosities η^* at frequency of 0.5 Hz of the compounds with different oil loadings are shown in FIG. 2. Herein, both the NR and NR/SBR blend compounds with DAE oil show the highest complex viscosities, while the TDAE and MES plasticized compounds show lower and almost the same values. The filled-NR compound without oil shows a lower complex viscosity when compared to the one with oil 5 phr; FIG. 2(a), but further increase of oil loading thereafter reduces the complex viscosities. Increasing oil contents gradually reduce the complex viscosities of the NR/SBR blend compounds without a clear peak at 5phr loading. Again, DAE gives slightly higher values than TDAE and MES.

It is quite conspicuous that DAE gives the highest complex viscosities compared with TDAE and MES, vs. the lowest in the Mooney case. The different trend of Mooney viscosity and complex viscosity may be attributed to the totally different ranges of shear strain applied during the tests. The shear strain in the Mooney test is basically continuously growing to very high values, while the complex viscosity is a dynamic shear test with a low maximum strain of 7%. The complex viscosity can be decomposed into a real (η') and an imaginary (η'') part. The

real part is related to the steady state viscosity that measures the rate of energy dissipation, while the imaginary part measures the elastically stored energy[12,13], as represented in FIGs. 2(b) and 2(c) for NR, and 2(e) and 2(f) for the NR/SBR blend. The results show that the oils in all cases have more of an influence on the elastic component η″ and less on the viscous part η′, similar to the Mooney relaxation data. For all cases, the filled NR compounds with DAE-oil show slightly higher viscosities over the compounds with TDAE and MES. For the NR/SBR blend compounds, a significantly higher η″ of the blend with DAE-oil compared to the ones with TDAE and MES indicates an even stronger elastic response of this blend in the uncured state.

The increase in viscosity of the NR compounds with the first 5 phr oils added is apparently mainly coming from the elastic component η″, FIG 2(c). The NR/SBR compound without oil initially has a higher complex viscosity than the NR compound: FIG. 2(d), which difference underlines the extra mastication effect in the NR compounds. However, with increasing oil loadings, the complex viscosities of the NR/SBR blend compounds are reduced to a greater extent, compared with the NR compounds.

Payne effect.-Fillers incorporated in rubber compounds have an influence on both static and dynamic properties, in the vulcanized case the result of two co-continuous networks: the crosslinked elastomer network and the filler network. Besides the strain-independent contributions of the hydrodynamic effect of the fillers and the crosslinked network of the rubber matrix, the dynamic modulus (G*) shows also a strain dependency which is attributed to breakdown of filler-filler interactions. This stress softening known as the Payne effect plays an important role in the understanding of the reinforcement mechanism of fillers in rubber compounds, in the non-vulcanized state as well as after vulcanization.[14,15] The degree of the

filler-filler interaction can be derived from the difference in storage moduli (ΔG′) at low and high strains, i.e. G′(0.56%) – G′(100%). The 7% strain employed for the complex viscosity experiments before plays a crucial role in this context. It has been documented, that for carbon blacks of various sorts in a SBR/BR formulation, including the N300 series, the maximum energy dissipation due to breakdown and reformation of the filler network takes place around 7% strain, as could be derived from Payne effect measurements.[16,17]

Regarding the Payne effect of NR and NR/SBR masterbatches as respectively shown in FIGs. 3(a) and 3(b), DAE oil gives a higher Payne effect than the other two oils in both types of compounds, at every oil content, indicating stronger filler-filler interactions. The Payne effects of all masterbatches decrease with increasing oil contents, which correlates with decreasing filler-filler interactions. Increasing oil contents dilute the contacts between filler aggregates/agglomerates and so provide less interactions. The reduction of the Payne effect with increasing oil content in NR/SBR filled compounds is more pronounced when compared with that of the NR-filled compounds. The filled NR masterbatches with 5 phr oil again show a peculiar higher Payne effect when compared to the masterbatch without oil. As discussed above for the viscosities, the addition of 5 phr of oil lubricates the filled system and lowers the shear forces generated during mixing, when compared to the masterbatch without oil. So, the break-up of filler agglomerates into aggregates may happen to a lesser extent, resulting in a slightly poorer dispersion and higher filler-filler interactions. However, when higher amounts of oil penetrate into the interstices between rubber and filler, the interactions between mutual filler particles become weaker.

As mentioned before, DAE oil has a better compatibility with both NR and SBR rubbers in the mixing temperature range, than TDAE and MES. Therefore, DAE oil interacts

more intricately with the elastomer molecules and swellw the rubber to a greater extent, leaving less oil located in between the rubber-filler interface and between the filler aggregates. The filler-filler interaction is therefore higher in the case of DAE-plasticized masterbatches. Moreover, the DAE oil that shows a higher compatibility with both elastomer types than the other oils, results in lower Mooney viscosity and lower shearing forces during mixing, causing less disruption of the filler-filler interactions. TDAE- and MES-oils which have less compatibility with the elastomers, move to interstices between filler particles/aggregates, facilitate filler dispersion, reduce the interactions between the filler aggregates/agglomerates, and so lower the storage modulus especially at low strain.

The latter now also explains the shorter Mooney stress relaxation and the higher η'' for the DAE-containing compounds, observed in the complex viscosity tests. In a similar manner it is the result of the stronger filler-filler interaction imparted to the compound by the DAE. And the fact that at the shear strain of appr. 7% the carbon black filler interaction is excessively triggered by continuous breaking and restoration of filler-filler bonds.

It all shows that the compatibility of the oils with the various elastomers also has an impact on the dispersion and filler-filler interactions of the carbon black employed, as it manifests itself in the rheological properties of the compounds before vulcanization. For rubber processing, the Mooney viscosity test is still the most commonly employed method to determine the flow behavior of compounds. However, rubber compounds with the same viscosity are often found to process differently.[18] The Mooney viscosity is tested under large deformations as the rotor imbedded in the rubber rotates at constant speed of 2 rpm, imparting a shear rate of only $\pm 1\ s^{-1}$.[19] Under the large resulting deformation, contact points and temporary filler network structures in the system deminish causing softening of the compound.

DAE which can better dissolve in NR and SBR than the other types of oils, therefore results in lower Mooney viscosity. On the other hand, on testing at low strain of 7% for the complex viscosity, where the continuous formation and destruction of the filler-filler network is most prominently sensed, the materials are mostly influenced by the elastic response from the filler network and interactions between the various components.

CURE CHARACTERISTICS

The rheometer torque differences, as shown in FIG. 4, are commonly related to the level of cure. Both filled NR and NR/SBR compounds with DAE oil show a slight higher torque differences ($M_H - M_L$). Also in the vulcanized state the better compatibility of DAE and rubber still leads to higher filler-filler interactions, contributing to a higher modulus. Furthermore, DAE oil contains nitrogen-and sulfur-heterocyclic compounds that can additionally accelerate and further increase the level of cure.[20] Increasing oil contents result in a decrease of the torque difference due to the dilution and plastization effects on the rubber and its components, which results in a lower maximum torque (M_H).

DAE oil gives higher cure rate indices (CRI) in the NR compounds when compared to TDAE and MES at the same oil contents, and this CRI increases with increasing oil contents as shown in FIG. 4. This means that DAE oil accelerates the curing reaction slightly because of the presence of nitrogen- and sulfur-heterocyclic species in this oil.[20] The CRI of the NR compounds with TDAE oil are further marginally higher than those for the compound with MES oil, as the MES is the most inert oil type due to its highest paraffinic content. For the NR/SBR blends the CRI decreases with higher oil contents, whereby the differences between the various oils are very small.

MECHANICAL PROPERTIES OF THE VULCANIZATES

The change of oil types by replacing DAE- with TDAE- and MES-oils has only minor effects on the mechanical properties of the NR vulcanizates, but shows more influence on the NR/SBR blend. The increase of oil loading to 10 and 15 phr results in lower tensile strength, but higher elongation at break, as shown in FIG. 5.

Increased oil contents especially to 15 phr lowered the cure torque difference (M_H-M_L), as previously shown in FIG. 4, which implies a lower crosslink density either by physical or chemical influences or both. The addition of higher oil content dilutes the contact points between polymer chains and filler aggregates, resulting in less resistance to deformation, but higher ultimate strain. The mechanical properties of the filled rubber vulcanizates are further mainly affected by the filler loading and filler dispersion level. Basically, a good dispersion of reinforcing fillers improves all fundamental properties of the rubbers. The change of the oil types causes no significant changes in the tensile properties of the carbon black filled NR compounds, but results in some change in the properties of the NR/SBR blend.

The results of abrasion tests of the vulcanizates are given in FIG. 6. The replacement of DAE with MES at every oil content results in an improvement of abrasion resistance of the NR vulcanizates, while the use of TDAE oil shows more or less the same level of abrasion resistance compared to the use of DAE oil. Increasing oil contents overall reduce the abrasion resistance of the NR vulcanizates, as reflected in an increase of volume loss in FIG. 6(a). The presence of oils in between rubber molecules and on the rubber-filler interface soften the vulcanizates and consequently increases the loss of rubber while being abraded. On the other hand, the addition of oils in filled-NR/SBR compounds improves the abrasion resistance of

these vulcanizates as observed in the lower volume loss, as shown FIG. 6(b). The lowest volume loss is observed when 5 phr of oil was added. Increasing oil contents to 10 and 15 phr deteriorate the abrasion resistance of the vulcanizates, but the volume loss is still lower than that of the sample without oil. When compared to the use of DAE oil, the NR/SBR blend vulcanizates with MES oil show only a slightly better abrasion resistance, but the use of TDAE oil drastically improves the abrasion resistance as expressed in the reduced volume loss of the NR/SBR blend vulcanizates at every oil content. The improvement of abrasion resistance of the NR/SBR blend in the presence of oils when compared to the unplasticized one might be attributed to a better homogeneity in the material and a better flexibility of chains. However, the increasing oil loadings soften the material causing the increased volume loss of rubber. Abrasion loss is a complex behavior of materials that is affected by various factors and is closely related to viscoelastic properties. In the NR/SBR case, the situation is even more complicated due to the presence of the binary rubber phases in which each phase has different filler affinity and oil compatibility.

As demonstrated in our earlier paper, the addition of oils had an influence on the glass transition temperature (T_g) of unreinforced NR and SBR compounds.[20] The use of DAE oil increased the T_g's of both rubber types, while the addition of TDAE increased the T_g of NR but slightly decreased the T_g of SBR. The addition of MES had almost no effect on the T_g of NR but reduced the T_g of SBR. The use of DAE-, TDAE- and MES-oils which have different T_g's is also expected to result in a shift of the T_g of the carbon black-filled compounds. The use of MES which itself has the lowest T_g among the three types of oils studied, should also result in the lowest T_g of the carbon black-filled compounds. The change of T_g does affect the viscoelastic behavior of the materials. Generally, rubbers with lower T_g have a better abrasion

resistance due to their good elastic behavior. The MES-containing NR compounds with the lowest T_g therefore show somewhat better elastic properties, as reflected in the better abrasion resistance and fatigue life: FIG. 6(a), when compared to the compounds with DAE oil. The influence of T_g of rubber on abrasion resistance has previously been reported[21], in the sense that a higher T_g resulted in higher DIN abrasion loss. The present results are in agreement with that. Furthermore, the MES oil contains a high paraffinic portion and waxes, and therefore the incompatible oil-components and waxes may migrate to the sample surface and affect the abrasive wear.[8] By combined effects of the lower T_g and the incompatible oil-components that may migrate to the surface, the use of MES oil in the NR compounds results in the lowest abrasion volume loss. However, a different behavior is observed in the NR/SBR blends in which the TDAE gives a lower volume loss than MES. The blend with TDAE oil thus has a better balance between good filler dispersion and a small change in T_g value of the SBR phase that provides the better abrasion resistance compared to NR.

Factors that influence the fatigue life of rubber vulcanizates include effects of mechanical loading history, environmental effects, rubber formulation and dissipation aspects of the constitutive response of rubber.[22] The addition of oil to the NR compounds tends to decrease the fatigue-to-failure properties of the vulcanizates especially in the case of DAE oil, as shown in FIG. 6. With 10 and 15 phr of oils, the NR compounds with DAE oil show significantly lower fatigue life when compared with TDAE- and MES-oils, which otherwise show similar results. The DAE-containing NR showed higher Payne effects, so stronger filler-filler interactions when compared to the other compounds. This will have a negative effect on the fatigue life under the displacement controlled test. The highest T_g of the DAE oil among the oil types studied will also affect the T_g of the filled-rubber vulcanizates to some extent.

The shift of T_g to higher temperature affects the stiffness and hysteresis of the rubber, and thus results in a poorer fatigue life.

Contrary to NR, the fatigue life of filled NR/SBR vulcanizates shows an increase after the addition of oils and with increasing oil contents, which can be ascribed to a better homogeneity of the blend and better filler dispersion. The presence of two rubber phases in the NR/SBR blend introduces an additional complication. SBR rubber has bulky phenyl groups in the styrene moieties which hinder rotation of the polymer backbone[23], and therefore gives high viscoelastic energy dissipation during deformation that positively affects fatigue life. The blends with TDAE oil show the best fatigue life. Like in the case of filled NR vulcanizates, the use of DAE-oil with the highest T_g in the NR/SBR blend results in the lowest fatigue life, the result of several contributions: its highest filler-filler interactions (FIG. 3) and the shift of T_g's of both rubbers to higher temperatures. Furthermore, the smallest difference in solubility parameters ($\Delta\delta$) between DAE and both NR and SBR makes them most compatible with each other and, consequently DAE reduces the strength of the rubber network of NR/SBR to a greater extent.[4] The good oil-rubber compatibility will also affect the elastic modulus and dynamically stored energy, and finally have an influence on specimen fracture. A study with ethylene propylene diene rubber (EPDM) by Jerrams et al.[24] showed that the fatigue life of rubber decreased in proportion to the degree of swelling. Greater swelling decreased the stiffness of the materials, and consequently increased the dynamically stored energy in the sample, which finally lead to failure.

Rebound resilience and heat build-up of NR and NR/SBR vulcanizates with different oil types and contents are illustrated in FIG. 7. As expected, increased oil contents, which is a viscous component, in the compounds decreases the rebound resilience of the vulcanizates: a

higher energy loss during deformation. However, increasing oil contents also give reduction of the heat build-up of the vulcanizates. The addition of carbon black into a compound commonly increases the heat build-up as a result of breakage of the carbon black filler-network structure and consequent viscoelastic loss.[25] The oil molecules distributed in the free volume between the rubber molecules and at the filler-rubber interfaces do loosen the filler-network and help to dissipate the heat and so cause less temperature rise in the rubber vulcanizates. The changes of rebound resilience and heat build-up as functions of oil contents and types of the filled NR vulcanizates are similar to the filled NR/SBR blends. That is, replacement of DAE with TDAE and MES in both NR and NR/SBR compounds gives some higher resilience and lower heat build-up, indicating some but little improvement in rubber elasticity.

DYNAMIC MECHANICAL PROPERTIES OF THE VULCANIZATES

The process oils have different glass transition temperatures, so the T_g's of the rubber compounds are also affected. The T_g's of unfilled NR- and SBR-vulcanizates were shifted according to the T_g's of the oils, as mentioned earlier.[20] For the carbon black reinforced NR compounds, the T_g's of all vulcanizates with varying oil types and contents are presented in FIG. 8(a). The T_g of the NR vulcanizate is practically not affected by the T_g of the oils; the shifts are smaller than 2°C as shown by the difference of T_g (ΔT_g) in relation to the unplasticized compound in FIG. 8(b). Addition of TDAE and DAE in the NR compounds slightly increases the T_g of the vulcanizates when compared to the one without oil, while the use of MES oil results in a marginal decrease. Increasing oil contents show no clear influence on T_g of the vulcanizates. When considering the filled NR/SBR blend vulcanizates, they

exhibit two T_g's associated with each blend component. The T_g's of NR and SBR in the blends with varying oil types and contents are plotted in FIG. 9(a), and the ΔT_g in relation the unplasticized compounds are shown in FIG. 9(b). The addition of all oil types results in increased T_g's of the NR and SBR phases when compared to the T_g's of the rubbers without oil, but the extent of changes is different. A smaller T_g-shift in NR is observed and no clear trend with oil contents and types. The shift of T_g for the SBR phase is larger. This T_g-shift is a combined result of, on the one hand, uneven carbon black distribution as it prefers the SBR phase,[21, 26-27] on the other hand, based on the T_g-shift in the NR and SBR phases, it indicates that the oils are preferentially located in the SBR- over the NR-phase. A study on oil distribution in blends of NR/SBR by Naito et al.[28] also showed that aromatic oil was favorably distributed towards the SBR phase.

The loss tangent (tan δ) values at 0°C and 60°C of the filled rubber-compounds are often used to indicate wet grip and rolling resistance for tires, respectively. The NR-vulcanizates with the three different oil types show almost identical values of tan δ at 0°C, while the NR/SBR blends with DAE and TDAE also show almost identical tan δ values at 0°C but higher than for the MES-plasticized vulcanizates: FIG. 10(a). Consequently, among the three types of oils studied, MES oil would indicate the lowest wet grip for the NR/SBR blends. The tan δ values at 0°C generally increase with raising oil contents due to the larger viscous contribution from the oils. Therefore, the incorporation of process oils generally improves the wet grip performance of tires. The NR/SBR blends further show a significantly higher tan δ at 0°C than pure NR due to the damping behavior of the styrene in the SBR blend component.

The loss tangent at 60°C of filled NR and NR/SBR vulcanizates are shown in FIG. 10(b).The NR and NR/SBR blend vulcanizates with DAE oil show a higher tan δ at 60°C

when compared with the rubbers with TDAE and MES, again due to its T_g influence. However, in this higher temperature regime there are apparently more factors involved in the energy storage and loss during deformation. These include filler dispersion, filler-filler and filler-rubber interactions. The higher loss tangent at 60°C for the DAE-containing vulcanizates correlates with its higher Payne effect (FIG. 3). Furthermore, the better compatibility between DAE and both NR and SBR, which results in a larger degree of swelling of oils in the rubbers, is also expected to increase the energy loss in the rubbers during cyclic deformation. From these results it may be inferred that the replacement of DAE- with MES- and TDAE-oils leads to a slightly lower rolling resistance if applied in tire treads. Increased oil contents improve wet grip but deteriorate tire rolling resistance. Based on these dynamic mechanical properties, the use of TDAE-oil provides the best balance of wet grip and rolling resistance for tire treads.

CONCLUSIONS

TDAE and MES oils as alternatives for conventional DAE oils possess different characteristics and so differs their influence on the properties of rubber compounds. The DAE-containing rubber compounds have lower Mooney viscosities but higher complex viscosities when compared with the compounds with TDAE- and MES-oils. The viscosities decrease with increasing oil contents, except for NR-compounds with 5 phr of oils where the values are higher than for the unplasticized compound due to an extra mastication effect of the NR without oil added during mixing. The use of DAE results in the highest Payne effect in both the NR and NR/SBR compounds before vulcanization. It indicates higher filler-filler interactions due to the highest compatibility of DAE with NR and consequently a larger plasticizing effect, which in turn enhances the tendency of carbon black aggregates to enter

into filler-filler interactions; but increasing oil contents reduce these filler-filler interactions again. The compounds with different oils show similar cure characteristics, but increasing oil contents lower the torque difference (M_H-M_L). The replacement of DAE- with TDAE- and MES-oils in the rubber compounds has no significant effect on the mechanical properties, but does influence the dynamic mechanical properties as a result of the different T_g's of the oils that affect the T_g of the compounds. The replacement of DAE with TDAE and MES improves the elastic properties of the filled NR as well as of the filled NR/SBR blend as indicated by an increased rebound resilience, decreased heat build-up and reduced loss tangent at 60°C.

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CAPTIONS FOR TABLES

TABLE I FORMULATIONS FOR THE COMPOUND STUDIES

CAPTIONS FOR FIGURES

FIG. 1.- Mooney viscosities and Mooney stress relaxation of HAF-filled compounds with varying amounts of DAE-, TDAE- and MES-oils: (a) NR and (b) NR/SBR.

Fig. 2.- Complex viscosities (η*), real (η') and imaginary (η") parts of η* of the HAF-filled compounds with different oil types and contents at 0.5 Hz at 7% strain and 100°C: (a-c, top row) NR and (d-f, bottom row) NR/SBR.

FIG. 3.- Payne effects of HAF-filled NR (a) and NR/SBR (b) masterbatches with various oil types and amounts.

FIG. 4.- Torque difference and cure rate indices at 150°C of HAF-filled (a) NR and (b) NR/SBR compounds with varying amounts of DAE-, TDAE- and MES-oils.

FIG. 5.- Tensile strength and elongation at break of HAF-filled (a) NR vulcanizates and (b) NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

FIG. 6.- DIN abrasion loss and fatigue life of HAF-filled (a) NR vulcanizates and (b) NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

FIG. 7.- Resilience and heat build-up of HAF-filled (a) NR and (b) NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

FIG. 8.- Glass transition temperatures (Tg) (a) and ΔT_g (b) in relation to the unplasticized compound of HAF-filled NR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

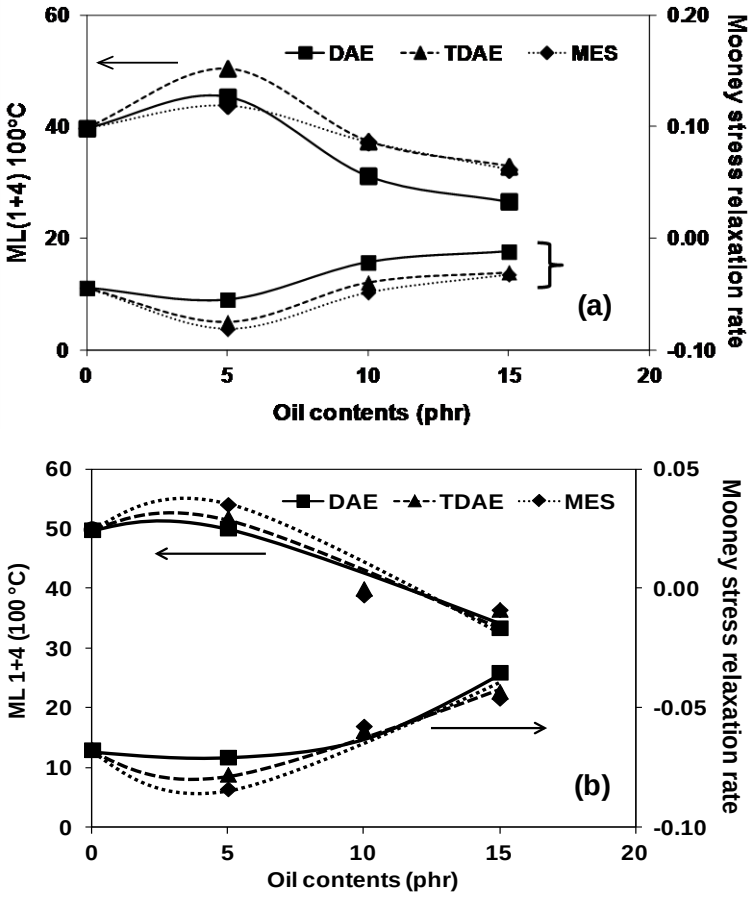
FIG. 9.- Glass transition temperatures (Tg) (a) and ΔT_g (b) in relation to the unplasticized compound of NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

FIG. 10.- Loss tangent at 0 and 60 °C of HAF-filled NR and NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils: (a) loss tangent at 0°C and (b) loss tangent at 60°C.

TABLE I

FORMULATIONS FOR THE COMPOUND STUDIES

Ingredients	Amount (phr)	
NR (RSS 3)	100.0	50.0
SBR (1502)	-	50.0
Carbon black (N330)	60.0	60.0
Oil: DAE, TDAE or MES	0, 5, 10 and 15	
Zinc oxide	3.0	3.0
Stearic acid	1.0	1.0
6PPD	1.5	1.5
TMQ	2.0	2.0
Microcrystalline wax	0.5	0.5
CBS	1.2	1.2
DPG	0.3	0.3
Sulfur	1.5	1.5



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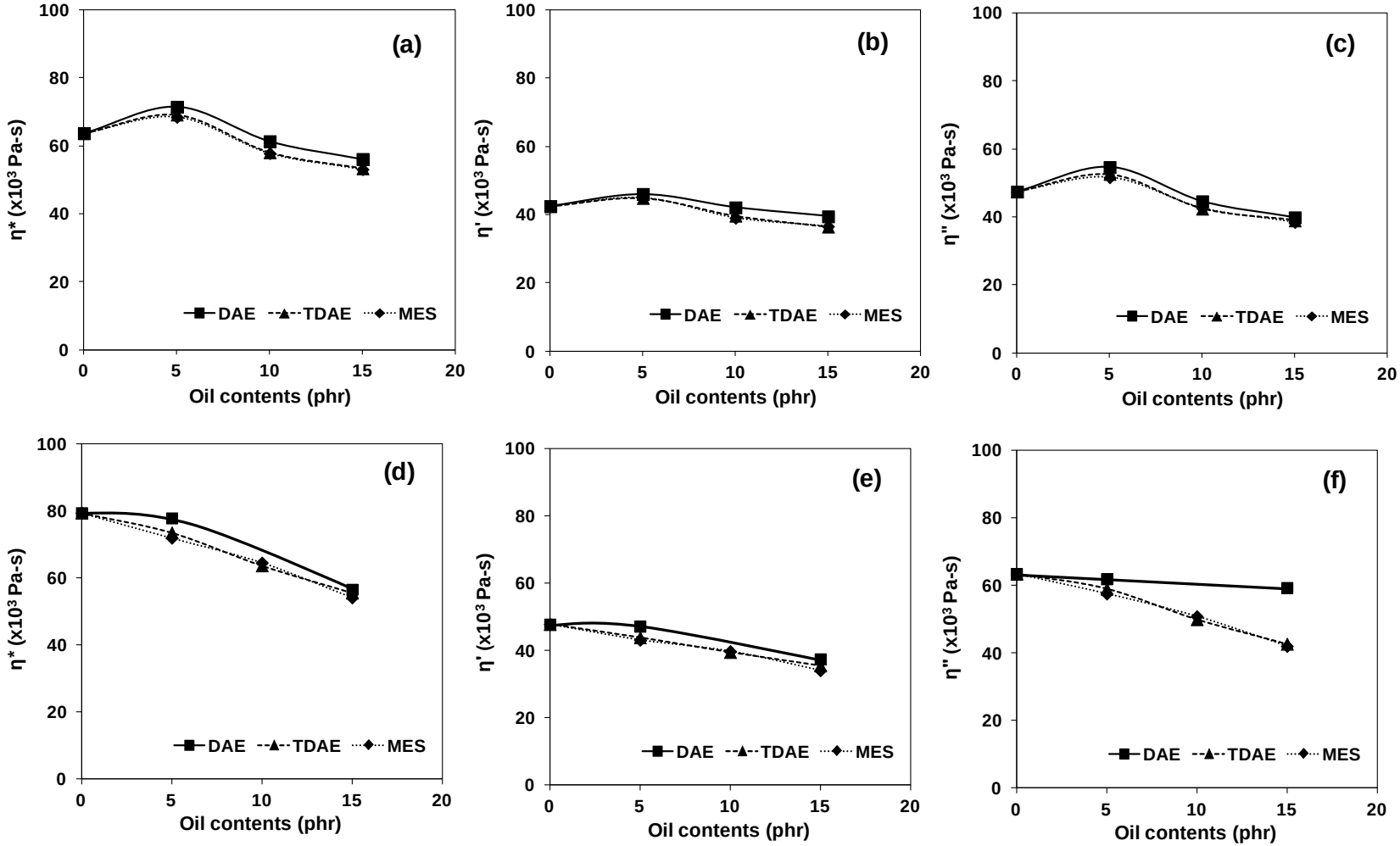

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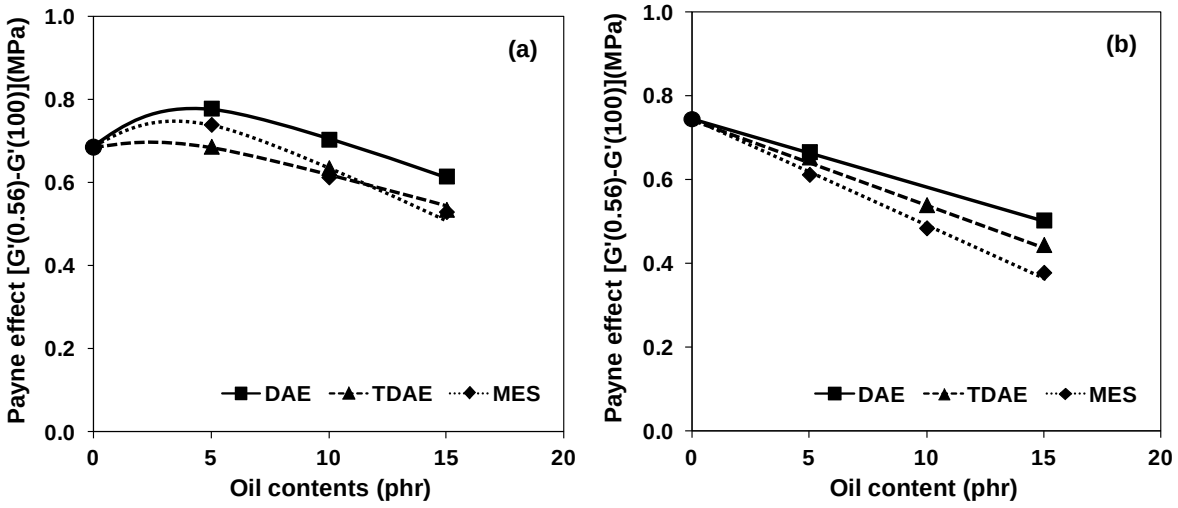

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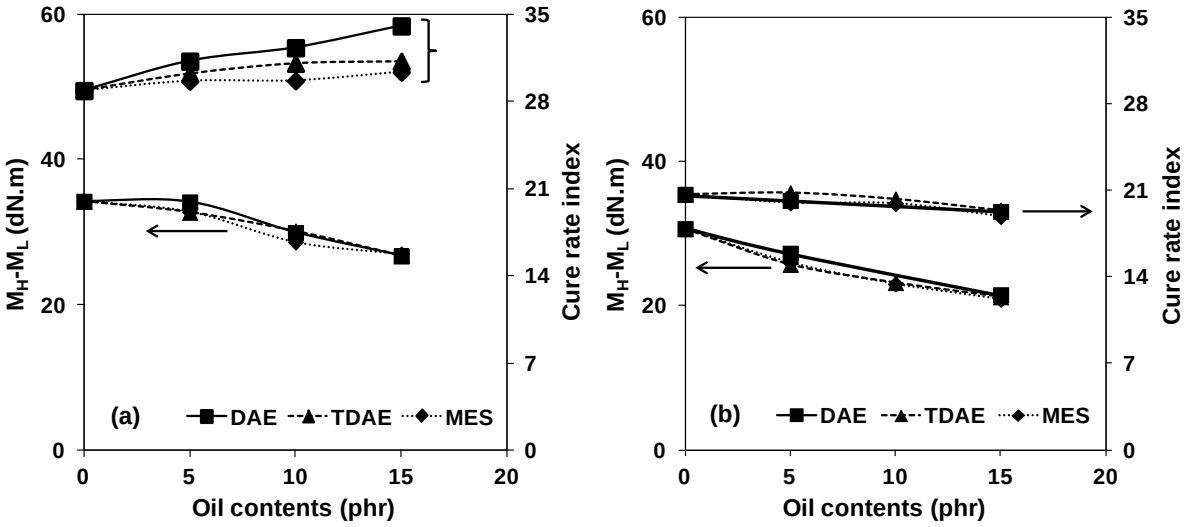

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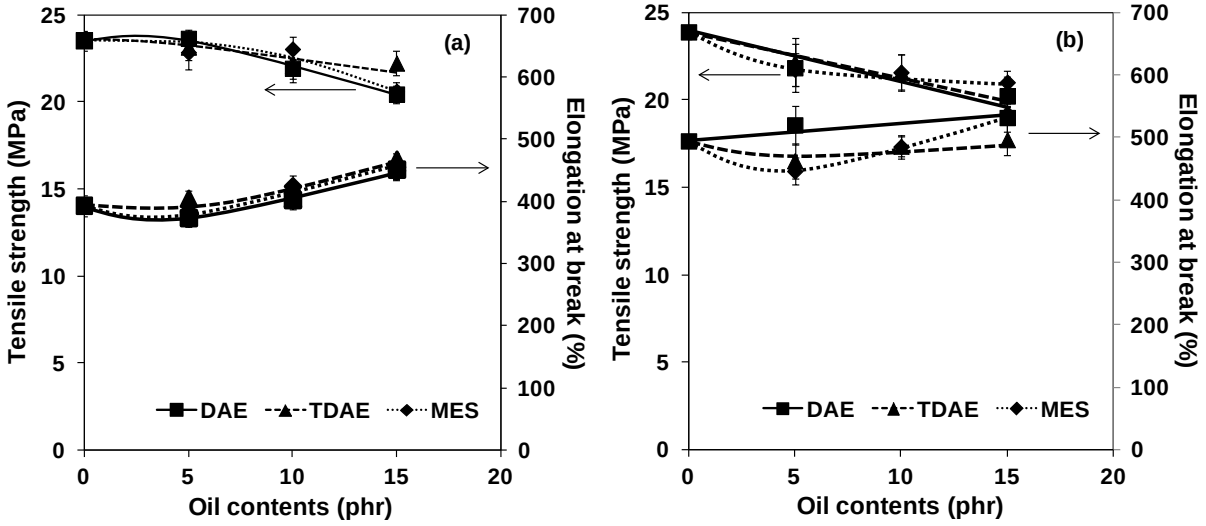

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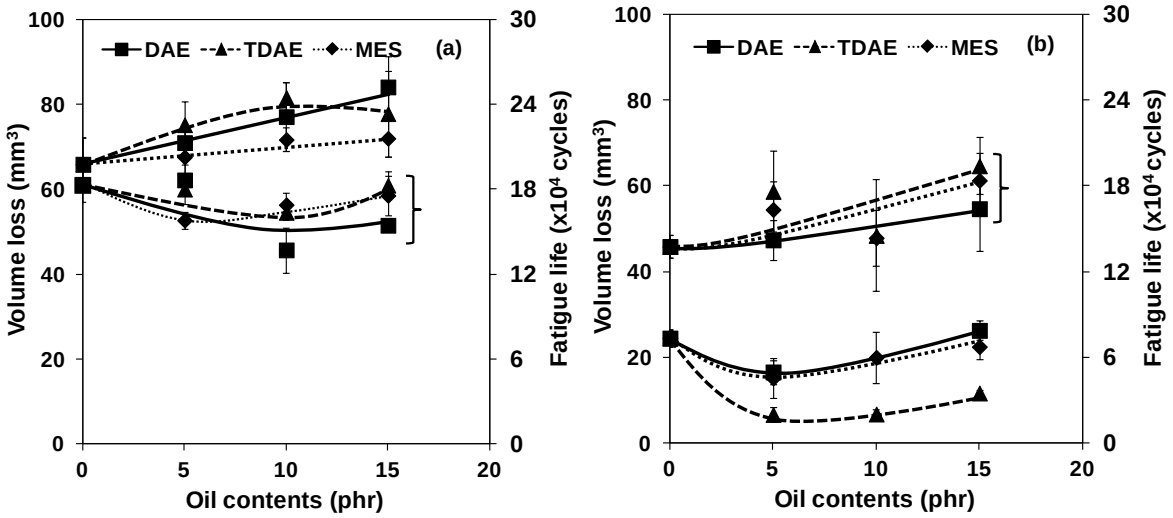

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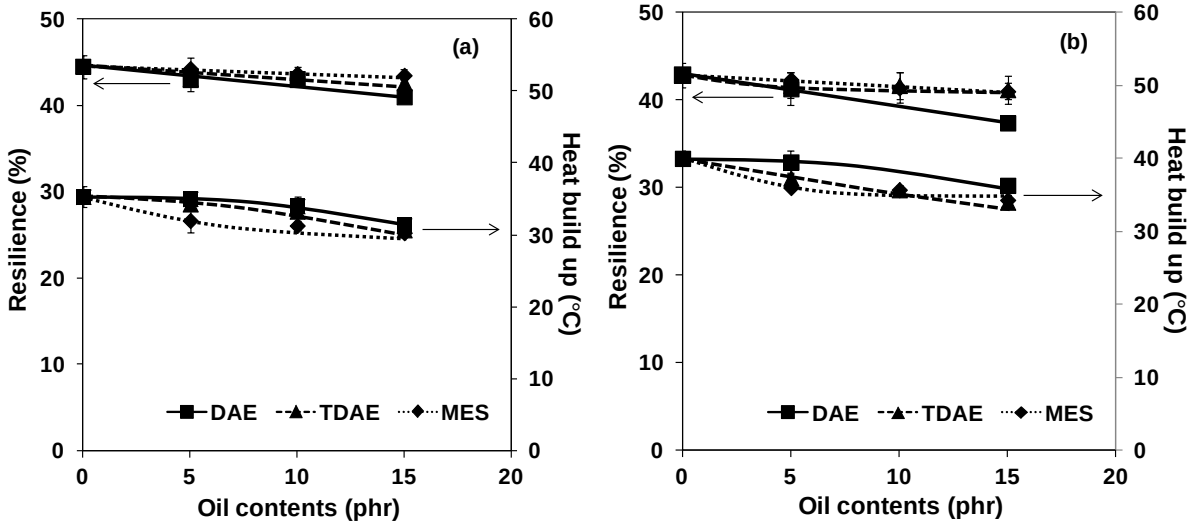

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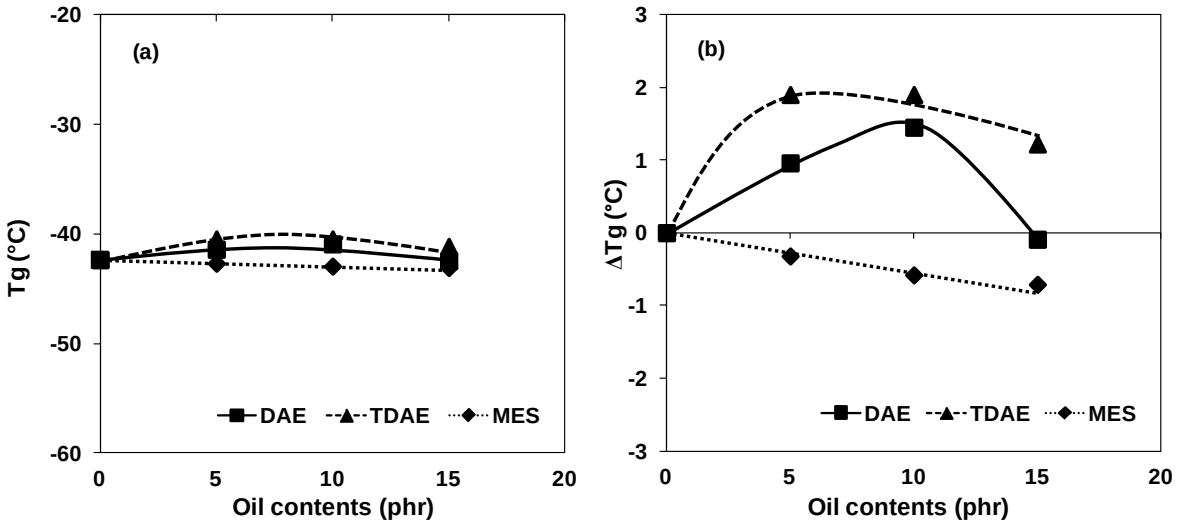

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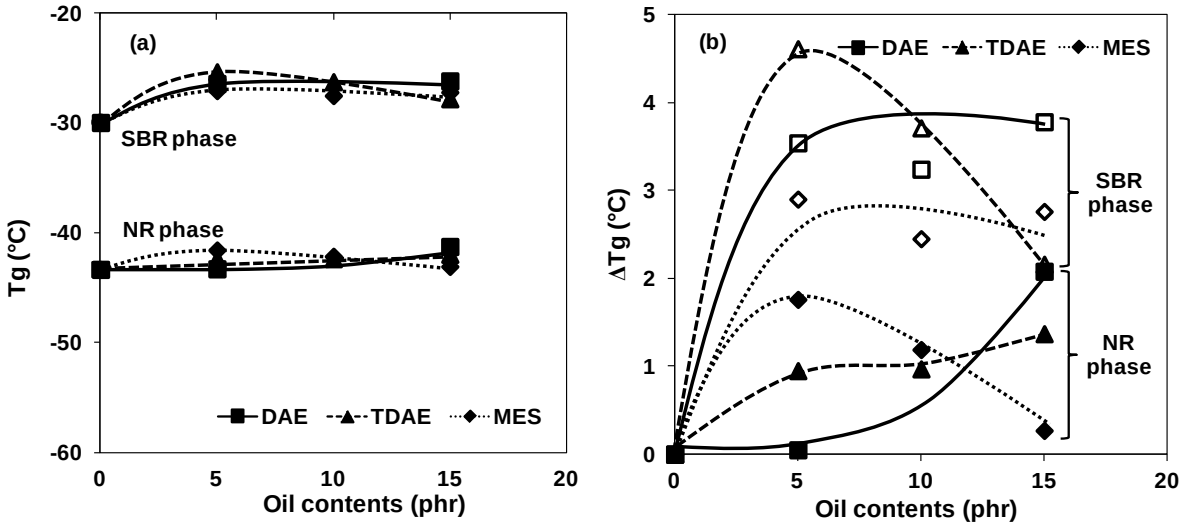

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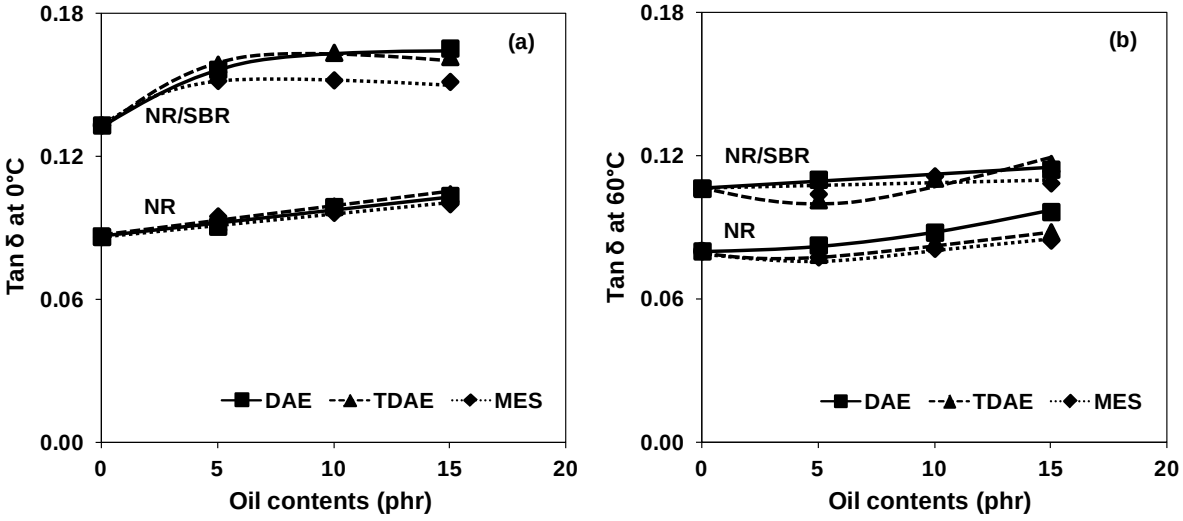

FIG. 10.- Loss tangent at 0 and 60 °C of HAF-filled NR and NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils: (a) loss tangent at 0°C and (b) loss tangent at 60°C.